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(54) **FORMULATIONS D'AEROSOL EN SUSPENSION**
(54) **SUSPENSION AEROSOL FORMULATIONS**

(57) Formulations pharmaceutiques d'un aérosol en suspension, contenant une dose thérapeutique efficace d'un médicament, et du HFC 134a, du HFC 227, ou un mélange de ceux-ci.

(57) Pharmaceutical suspension aerosol formulations containing a therapeutically effective amount of a drug and HFC 134a, HFC 227, or a mixture thereof.

AM8

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METAL COATED PRODUCT

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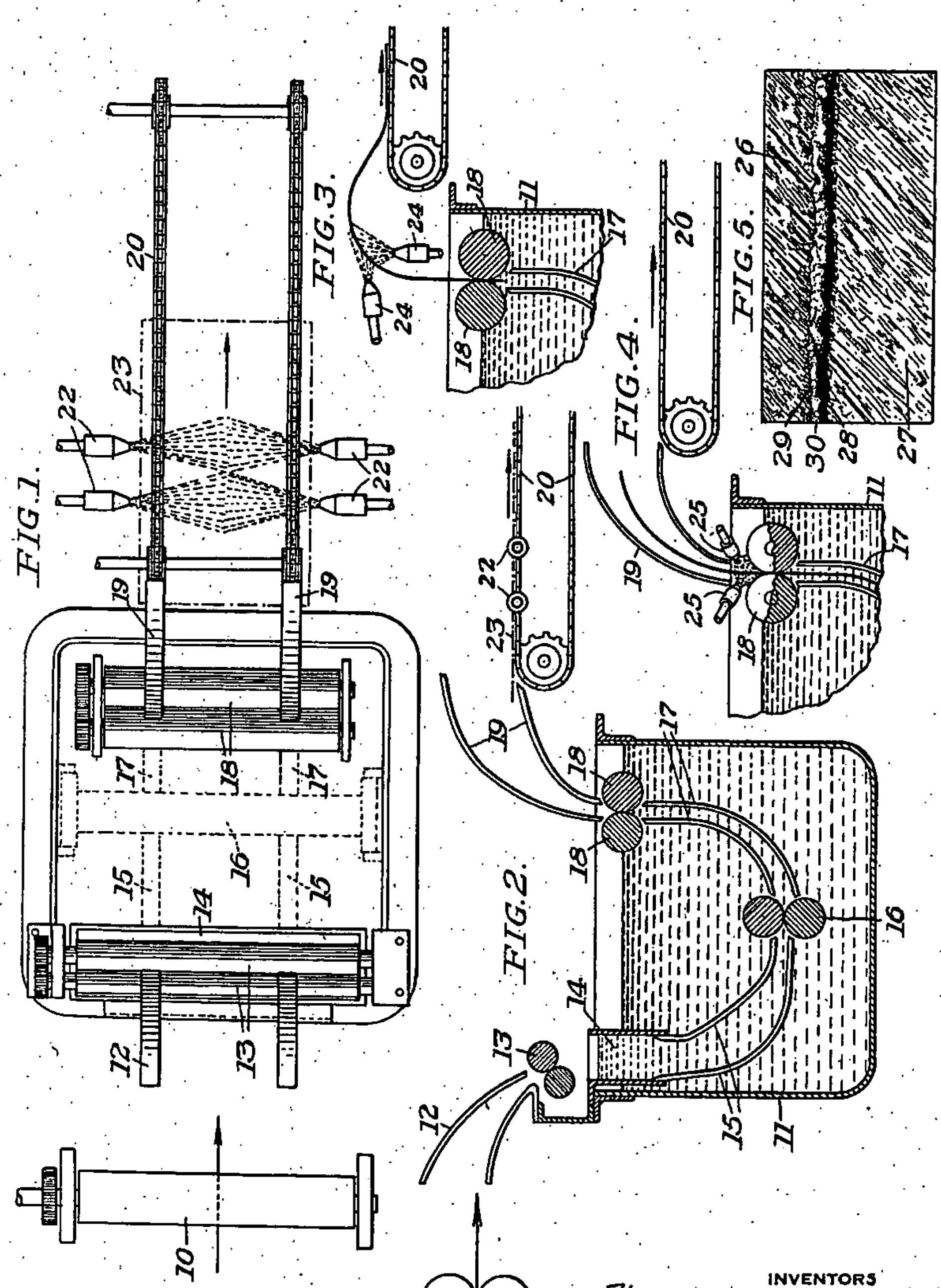

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UNITED STATES PATENT OFFICE

2,126,244

METAL COATED PRODUCT

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2 Claims. (Cl. 29—181)

This invention relates to metal coated products, and, while not specifically so limited, has particular application in respect of coated, and especially galvanized, sheet metal, such, for example, as steel sheets. Superior coated products, and particularly galvanized sheet steel products, are produced. This application is in part a division of our copending application Serial No. 12,398, filed March 22, 1935, which, in turn, is in part a continuation of our application Serial No. 741,222, filed August 24, 1934.

Purely for purposes of description and illustration the invention will be described as specifically embodied in galvanized or zinc coated steel sheets. Sheets of this character have wide commercial use. As ordinarily made they have both sides spangled, that is, the zinc coating in cooling forms over both surfaces of the sheet large heterogeneous crystals or spangles readily distinguishable to the naked eye even at some distance. For most purposes these spangled surfaces are not undesirable, and indeed they are definitely desirable in cases where a certain type of finished appearance is wanted.

However, for other purposes sheets having both surfaces spangled are definitely undesirable, as, for example, when the product is to be painted. Spangled galvanized surfaces will not take paint readily. It has been the practice heretofore to permit spangled galvanized sheets to weather, or to artificially weather them, as by treatment with acid or other chemical having the effect of oxidizing the surfaces of the sheets, in order that the surfaces to be painted may become somewhat roughened so that paint will readily adhere thereto.

We have discovered that galvanized sheets may be produced without the ordinary spangled surfaces, without the undesirable buckling of the sheets which has attended previous efforts to produce unspangled galvanized sheets, and with a smooth dull matte or slightly roughened surface which is at the same time highly resistant to corrosion, beautiful in appearance and readily receptive to paint and other similar coating materials. We are well aware of the previous efforts which have been made along these lines in both the practical and the patented art, but no product having the features and advantages of our product has heretofore been proposed and no finish having the desirable qualities of our finish has heretofore been produced.

Before proceeding to explain our invention we wish it understood that we do not claim broadly to have invented the formation of unspangled galvanized metal surfaces, as unspangled surfaces have been produced before. One way in which unspangled galvanized surfaces have been produced is by dipping the hot galvanized ware as it comes from the galvanizing pot into a liquid bath, which prevents the formation of spangles, produces a mottled, irregular, partly bright and partly dull surface and results in warping the ware due to the rapid and uneven temperature changes brought about by the dipping. The warping can be reduced to some extent by heating the bath in which the ware is dipped, but, aside from the question of warping, the finish is unsatisfactory in appearance, is not highly resistant to corrosion and will not take paint readily. It has also been proposed to subject galvanized ware to the action of a jet of water or other liquid, but this has substantially the same results as dipping. The finish produced is not uniform, being partly bright and partly dull and mottled, is not highly resistant to corrosion and will not take paint satisfactorily. Furthermore, the subjecting of the hot galvanized ware to a jet of liquid results in warping of the ware as in the case of dipping.

After considerable experimenting we have discovered that the highly desirable unspangled, uniform, dull matte finish may be produced by subjecting the galvanized ware (here considered for purposes of illustration as comprising sheets) to the action of a mist or very fine spray. The mist or very fine spray is to be clearly distinguished from the jet of liquid referred to above, as the results obtained by the two processes are entirely different. The sheets after leaving the galvanizing bath are brought into the presence of the mist or very fine spray before the large spangles characteristic of ordinary galvanized ware have formed. Almost immediately upon leaving the galvanizing bath the zinc coating begins to cool and crystallization commences. If this crystallization is allowed to progress unhindered the large spangles characteristic of ordinary galvanized ware will be produced. By bringing the hot sheets into the presence of the mist or very fine spray we prevent the formation of the large spangles and the desired uniform dull matte finish results.

While we are not certain as to the theory underlying the process above described, we think that the fine particles of the mist exert a physical effect on the surface of the sheet, creating relatively very closely spaced centers of propagation or crystallization from which the crystals form. But when the centers of propagation of crystals

are relatively closely spaced the crystals are of relatively small size as adjacent crystals during propagation come in contact with each other before the crystals can attain relatively large size, resulting, as it were, in the squeezing into the same surface area of a relatively very great number of relatively very small crystals which, due to the relative proximity of their centers of propagation or crystallization, have had no opportunity to grow to or even to approach the size of what are commonly known as "spangles", which are readily distinguishable to the naked eye even at some distance and which may in some cases extend from their respective centers of crystallization for a distance of an inch or more in various directions. If the size of the crystals is properly controlled the sheet will appear to the naked eye to have a uniform continuous dull matte surface. Under a powerful magnifying glass this surface will be seen to be crystalline, presenting an appearance similar to an ordinary spangled surface. However, the relatively great number of relatively small, relatively closely spaced crystals affords an ideal surface for the reception of paint and similar coatings, and this surface is also particularly well suited for various uses without painting or covering with similar coatings, as, for example, for oven linings.

We have found that by appropriately controlling the mist or spray and the passage of the sheet in relation thereto we can form a sheet having one side spangled in the characteristic manner and the other side provided with the uniform dull matte finish above described. Sheets of this character are highly desirable and useful. For example, they may be used for signs, such as advertising and highway direction signs, paint being applied to the side provided with the dull matte finish to form the front of the sign, and the back of the sign being left unpainted. The ordinary spangled finish of the back of the sign effectively withstands corrosion so that a highly satisfactory yet relatively inexpensive sign is thus produced. Another use to which sheets having one side spangled in the usual manner and the other side provided with the uniform dull matte finish may be put is in the construction of refrigerator cases. The side having the dull matte finish forms the outside of the case and receives the usual white enamel paint, while the spangled side faces toward the interior of the refrigerator and is naturally well adapted to withstand corrosion due to moisture within the refrigerator. Sheets of this character may also be used for oven linings, the unpainted dull matte finish facing the interior of the oven.

Various materials may be used for producing the mist or very fine spray. Plain water alone if sufficiently finely divided is fairly satisfactory. Using a fine mist of plain water does not, however, give as exact control of surface appearance as is desirable for many purposes. However, we have found that water solutions of certain chemicals produce markedly superior results. A few of the chemicals thus used listed approximately in the order of efficacy are copper sulphate, sodium nitrate, sodium chloride, potassium chromate and potassium permanganate. These salts are precipitated rapidly from their water solutions at temperatures slightly above the solidifying point of zinc or the zinc alloys usually employed for galvanizing. The solidifying point of the galvanizing material may be in the neighborhood of 760° F. to 800° F. While we are not certain as to the theory of action, we believe that the rapid evaporation of the water results in the almost immediate precipitation or deposition on the surface of the sheet of microscopic, almost unmeasurably small particles of the salt or of some precipitate formed upon the application of heat to the mist composed of the salt solution. This precipitate seems to have the effect of controlling the centers of propagation of the crystals so that such centers are distributed quite uniformly over the surface of the sheet and very close together. Apparently those substances whose solutions most quickly deposit their precipitates on the surface of the sheet upon the application of heat in the neighborhood of the temperatures mentioned above are most satisfactory for our purpose.

Care must be taken to keep the mist very finely divided. If a relatively coarse spray or jet is used the sheet will either appear spangled or it will have a non-uniform mottled appearance, being partly bright and partly dull, and the surface will not be as suitable for painting as is the uniform dull matte surface produced by our process.

Other features, details, objects and advantages of the invention will become apparent as the following description of certain present preferred methods of treatment of coated sheets, certain present preferred apparatus for carrying out the method and producing the desired product and a present preferred form of product proceeds.

In the accompanying drawing we have shown certain present preferred forms of apparatus for producing coated sheets and a present preferred form of product, in which:

Figure 1 is a plan view of one form of apparatus;

Figure 2 is an elevational view, partly in vertical longitudinal cross section, of the apparatus shown in Figure 1;

Figures 3 and 4 are each a detail elevational view, partly in vertical longitudinal cross section, of a portion of a modified form of apparatus; and

Figure 5 is a view made from a photomicrograph showing in cross section a portion of a mounted coated sheet.

The steel sheets which are to be coated are first treated to remove dirt and scale, as, for example, by pickling, blasting, etc. This step may be omitted if the sheets are originally clean. The sheets are then treated in apparatus as shown in the drawing and now to be described.

Referring now more particularly to Figures 1 and 2, a set of feed rolls 10 is located adjacent the entrance of a galvanizing pot 11 of known construction and provided with entry guides 12 and feed rolls 13 by which sheets advancing through the feed rolls 10 are directed downwardly into the pot 11 through a flux bath 14 floating on the surface of the molten zinc or spelter contained in the pot 11. Guides 15 direct the sheets through the spelter between bottom rolls 16. Guides 17 extend from the rolls 16 upwardly toward the exit rolls 18. As the sheets pass between the rolls 18 they are engaged by exit guides 19 which deliver them onto a conveyor 20 or other transporting means.

When the form of apparatus shown in Figures 1 and 2 is used the sheets are subjected to a mist or very fine spray as they are carried along by the conveyor 20. The mist or spray is indicated in Figure 1 by reference numeral 21 and is created by means of very finely adjusted spray nozzles 22 connected with a supply of the fluid being sprayed and a suitable source of spraying pres-

sure. We have found that in order to produce a sufficiently fine spray or mist to enable most satisfactory accomplishment of the desired results a source of spraying pressure in addition to the pressure of the fluid being sprayed should be employed. The most convenient source of spraying pressure is compressed air. The fluid may be effectively atomized by the use of compressed air, any suitable atomizing device being used. The position of a sheet on the conveyor 20 is indicated at 23. With this form of apparatus the spray impinges on both sides of the sheet. The nozzles may, however, be so positioned as to direct the spray against one or both sides of the sheet. The effect of the mist or fine spray is as explained above, resulting in the production of a dull silvery or matte finish in which the crystals are so small as not to be individually distinguishable by the naked eye.

The point at which the mist or spray impinges on the coated sheet may be varied within certain limits and the precise point at which the mist should impinge upon the sheet is dependent on various factors including the character and temperature of the spelter, the speed of movement of the sheet, the width and thickness of the sheet, the weight of the coating, the factor of whether the mist is applied to one or both sides of the sheet, etc. It is, however, important that the mist shall impinge upon the coated sheet before the process of crystallization has advanced far enough so that the production of crystals clearly distinguishable to the naked eye will result. As crystallization may not set in immediately upon delivery of the sheet from the spelter bath, particularly when a relatively heavy coating is applied, it is sometimes desirable not to treat the successive portions of the coated sheet with the mist until a predetermined time after such portions have emerged from the spelter. For example, a treatment such as that above described and illustrated in connection with Figures 1 and 2 allows a relatively great time interval before treatment of the sheets with the mist, although, of course, the greater the speed of the sheets the greater the distance from the point of emergence of the sheets from the spelter to the point of impingement of the mist thereon may be.

The apparatus shown in Figure 3 is similar in all respects to that shown in Figures 1 and 2 except for the positioning of the nozzles 24. These nozzles are arranged in two series extending transversely of the sheet and substantially opposite each other in the direction of movement of the sheet, the nozzles being directed so that the mist impinges on the sheet at an angle in the direction of movement of the sheet. It has been found that when the nozzles are so positioned superior results are obtained. The reason for this is not definitely known although it is believed that when the nozzles are directed so that the mist impinges on the sheet at an angle in the direction of movement of the sheet the effect is to more rapidly evaporate the mist particles without such a cooling effect as will produce spangles which may result if the nozzles are directed so that the mist impinges on the sheet at an angle in the direction opposite the direction of movement of the sheet. When it is desired to treat only one side of the sheet only one set of nozzles is operated, the other set being shut off. Also in Figure 3 the nozzles are spaced somewhat nearer the point of emergence of the sheet from the bath than in Figures 1 and 2. However, the exact position of the nozzles relative to the point of emergence of the sheet from the bath may be varied as desired in accordance with the factors above mentioned.

In Figure 4 a further modified form of apparatus is disclosed, this apparatus likewise being the same as that of Figures 1 and 2 except for the positioning of the nozzles. In Figure 4 the nozzles 25 are positioned so as to spray laterally from one or both sides of the sheet, the spray impinging both on the sheet and also on the exit rolls 18. An arranement of this character is used on very thin sheets thinly coated in which crystallization tends to commence immediately upon exposure of the coating to the air.

Figure 5 is a reproduction of a photomicrograph at 250 magnifications of a cross-section through one form of product made in accordance with the present invention. The specimen is mounted on copper to enable its edge to be filed in preparation for photographing. The copper mounting is designated by reference numeral 26. The base member is shown at 27. Next the base member is a layer 28 comprising alloy of the metals of the base and coating. The surface of the product is designated at 29, there being at the surface a layer 30 of material comparatively free from the alloy above mentioned and predominantly of the metal of the coating. The surface of the product is characterized, as above explained, by the absence of crystals readily distinguishable by the naked eye. It is substantially the color of galvanized ware, although being dull instead of bright. The surface is slightly rough and characterized by its ability to readily receive and retain a non-metallic finish coating such as paint.

For example, when the product is a ferrous sheet coated with spelter, the base member 27 is the sheet itself and comprises ferrous metal, and the coating is a zinciferous coating. The layer 28, referring to Figure 5, comprises iron-zinc alloy, while the layer 30 is a zinciferous layer comparatively free from such alloy. Normally, the layer 30 is predominantly zinc and approaches in composition substantially pure zinc, although it may contain some iron-zinc alloy.

The line of demarkation between the layers 28 and 30 may be fairly well defined, depending upon the conditions obtaining in the manufacture of the product. Ordinarily, there will be a fairly well defined line of demarkation, as indicated in Figure 5, although the line of demarkation may not, and likely will not, be a straight line in a cross-section such as shown. However, it is to be borne in mind that the cross-section shown in Figure 5 is magnified 250 times.

Figure 5 may also be taken as representative of a cross-section through a painted coated product made in accordance with the present invention, although, of course, the coat of paint will not be as thick as the copper mounting 26. The paint does not substantially react with the coating, but is readily received and retained thereby. For example, the product, when in sheet form, may be used in the manufacture of signs, as, for example, highway warning signs and advertising signs, and it may be painted with an enamel or aluminum paint or with any ordinary type of paint.

One important advantage of the invention is that the necessity for heating the treating substance is eliminated, together with the consequent increased cost. Our treating substance may be applied at its natural storage or room temperature and does not need to be heated.

Apparently the very fine state of sub-division of the particles of the mist prevents the mist from having an undesirable cooling effect which might tend to buckle the sheet. Furthermore, the resistance to corrosion of the coated product does not appear to be substantially lower than the resistance to corrosion of an ordinary spangled galvanized sheet, which is noted for being highly corrosion resistant.

It is old to wipe the molten zinc coating applied to sheets by means of a steam jet. This does not, however, produce a product of the character in which we are interested. The effect of a jet of dry steam is to wipe the coating, while the effect of a jet of wet steam is to make the coating brighter and more or less non-uniform. Also, a cooling air blast has been applied to galvanized sheets on emergence from a zinc bath, but this treatment does not produce the uniform dull unspangled matte finish which we produce but rather tends to increase the brightness and spangled effect of the zinc coating. Our process does not result in wiping the coating and is effective on either light or heavy coatings.

While we have shown and described certain present preferred apparatus for and methods of carrying out our treatment and a present preferred form of product, it is to be distinctly understood that the invention is not limited thereto and is of relatively wide application to products other than sheets and may be otherwise variously embodied within the scope of the following claims.

We claim:

1. A metal coated sheet metal product comprising a ferrous sheet metal base with a zinciferous coating thereon, said product having a layer comprising iron-zinc alloy next the base and a layer at the surface thereof which is predominantly zinc and approaches in composition substantially pure zinc with a fairly well defined line of demarkation between said layers, such surface being characterized by the absence of crystals readily distinguishable by the naked eye and by a uniform homogeneous dull matte texture and being highly resistant to corrosion and readily receptive to finish coatings such as paint.

2. A metal coated sheet metal product comprising a ferrous sheet metal base with a zinciferous coating on both of the opposed faces thereof, said product having on one of said faces a layer comprising iron-zinc alloy next the base and a layer at the surface thereof which is predominantly zinc and approaches in composition substantially pure zinc with a fairly well defined line of demarkation between said layers, such surface being characterized by the absence of crystals readily distinguishable by the naked eye and by a uniform homogeneous dull matte texture and being highly resistant to corrosion and readily receptive to finish coatings such as paint, said product having on the other of said faces a spangled galvanized finish.

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